

X-ray Spectroscopy of Aqueous Salt Solutions

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We have performed measurements of the perturbation to the oxygen K-edge X-ray absorption spectrum (XAS) of liquid water induced by addition of various inorganic salts using liquid microjets. Systematic investigation of aqueous sodium halide solutions conclusively demonstrates that water-anion interactions have a considerable influence on the observed XAS spectra. There are, however, no ion specific effects observed that are associated with the addition of numerous monovalent cations (Li^+ , Na^+ , K^+ , NH_4^+ and $\text{C}(\text{NH}_2)_3^+$). In contrast, the addition of divalent cations (Mg^{2+} and Ca^{2+}) engender unique changes to the liquid water XAS. Density functional theory calculations indicate that the major factor that gives rise to both the anion and cation specific spectral changes is direct distortion of the unoccupied molecular orbitals of water molecules in the first solvation shell of the ion, which is negligible for the monovalent cations. Differences in the induced electronic distortion are primarily associated with the magnitude of charge transfer from (anions) or to (cations) the solvated ions. Spectral changes associated with geometric distortion of the hydrogen bonds formed by solvation shell water molecules (i.e. hydrogen bond “breaking”) are thought to be secondary.